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(71) Applicant(s)
Danisco A/S
(Incorporated in Denmark)
P.O.Box 17, Langelægade 1, DK-1001 Copenhagen K,
Denmark

(72) Inventor(s)
Jorgen Madsen

(74) Agent and/or Address for Service
D Young & Co
21 New Fetter Lane, LONDON, EC4A 1DA,
United Kingdom

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(54) Abstract Title
Non-pourable emulsion

(57) A non-pourable emulsion comprises: an aqueous phase comprising a citric acid ester of mono- and diglycerides of fatty acids; and a fat phase comprising a citric acid ester of mono- and diglycerides of fatty acids, wherein the fat phase is substantially free of lecithin and monoglycerides. The citric acid ester is preferably present in an amount of 0.1 to 3 % by weight of the emulsion. The fatty acids may have a chain length of from 4 to 24 carbon atoms. The fat phase preferably has no greater than 0.3 % by weight of lecithin and no greater than 0.2 % by weight of monoglyceride. The non-pourable emulsion is preferably an edible composition for frying.

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Edible Composition

The present invention relates to an edible frying compositions comprising a fat phase and an aqueous phase which composition comprises an anti-spattering agent. The
5 compositions are products which are non-pourable and may be filled in tubs or wrapped in paper/foil.

Edible compositions comprising a fat phase and an aqueous phase are well known frying media for shallow frying.

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In recent years consumer concern on health has increased and hence frying products which are not 100 wt% fat shortenings or oils but products that comprise a varying amount of water phase of up to about 60 wt% are used in shallow frying. Emulsified water in a frying product leads to spattering problems when such products are used in
15 shallow frying.

Spattering of a water in oil emulsion is believed to be caused by superheating of water droplets. At a certain point after heating water droplets explosively evaporate, whereby the product can be spread all over the surroundings of a frying pan in which the
20 emulsion is heated. This may cause danger to the person who fries foodstuff in the heated emulsion and it also often causes a mess in the kitchen.

It is known to add anti-spattering agents like lecithin or salt to frying products to reduce the spattering tendency.

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A survey of anti-spattering agents in margarine was given at the 16th ISF Congress, Budapest, 1983, Fat Science, pp. 499-506.

Alternative anti-spattering agents have been suggested for spreadable products. These
30 agents are usually combined with lecithin and include monoglycerides, phosphatides, citric acid esters of monoglycerides, and combinations of these.

RD 24152 discloses the use of citric acid esters and lecithin in a low fat spreadable product comprising about 52 wt% fat.

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RD 28364 discloses a 60% fat spread comprising a water phase and a fat phase. The water phase may contain a citric acid ester of saturated monoglycerides. This water phase may be combined with a fat phase containing a citric acid ester of a monoglyceride and either soya lecithin or a monoglyceride. The lecithin containing product is stated as having better frying properties than the monoglyceride containing product.

The present invention alleviates the problems of the prior art.

10 In one aspect there is provided a non-pourable emulsion comprising (i) an aqueous phase comprising a citric acid ester of mono- and diglycerides of fatty acids; and (ii) a fat phase comprising a citric acid ester of mono- and diglycerides of fatty acids, wherein the fat phase is substantially free of lecithin and monoglycerides.

15 Some further aspects of the invention are defined in the appended claims.

In the present specification, in one alternative, by the term "non-pourable" it is meant an emulsion having a Bostwick value of less than 7.

20 In the present specification, in a further alternative by the term "non-pourable" it is meant an emulsion having the following solid fat content (SFC) within the given ranges at each of the temperatures below

Temp., °C	SFC
5	9 - 72
10	8 - 56
20	6 - 31
30	0 - 24
35	0 - 15
40	0 - 10

25 In the present specification by the term substantially free of lecithin it is meant that lecithin is present in the fat phase in an amount of no greater than 0.3 wt% of the fat phase, preferably no greater than 0.2 wt%, more preferably no greater than 0.1 wt%.

In the present specification by the term substantially free of monoglycerides it is meant monoglyceride is present in the fat phase in an amount of no greater than 0.2 wt% of the fat phase, preferably no greater than 0.1 wt%, more preferably no greater than 0.05

wt%.

It has now surprisingly been found that a non-pourable emulsion may be provided which can be utilised in frying without the need to incorporate in the fat phase of the emulsion a monoglyceride or a lecithin as an anti-spattering agent. It has been found that emulsions absent monoglyceride and lecithin show similar to or even better anti-spattering performance as emulsions comprising one of these constituents. Without wishing to be bound by any theory, we believe that the citric acid ester may partly function as an emulsifier by settling at the interface between the water and the fat phase of the present emulsion.

The invention further relates to a process for the preparation of such frying products.

All concentrations in this specification are weight concentrations unless indicated otherwise.

Spattering can be measured by determining the spattering value according to the method illustrated in the examples. Preferably emulsions according to the invention show a primary spattering value, SV1, (spattering upon heating of a frying product such as margarine, without incorporation of a food product to be fried) of from 7 to 10, more preferably from 8.0 to 10. The secondary spattering value, SV2, (spattering upon incorporation of a food product such as meat in a shallow frying product) for products according to the invention is preferably from 5-10.

The emulsions according to the invention can be used in shallow frying of food stuff.

The emulsions according to the invention comprises citric acid ester of mono- and diglycerides of fatty acids. In the present specification, this ester or a mixture of such esters is also referred to as "citric acid ester".

30

The citric acid ester is preferably present in an amount of from 0.1 to 3 wt% on total product weight. A lower level may not show significant reduction in spattering and a higher amount may lead to taste defects.

35 Preferably the citric acid ester is present in the aqueous phase of the emulsion and the

interface between the aqueous phase and fat phase in an amount of from 0.07 to 3 wt% of the emulsion. Amounts below 0.07 wt% generally do not show the preferred improvement in spattering behaviour, although some improvement might be observed. Amounts above 2 wt% on aqueous phase can lead to taste defects.

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Citric acid (3-carboxy-3-hydroxypentanedioic acid) and fatty acid sources such as mono- and diglycerides of fatty acids, can form an ester under certain reaction conditions. The resulting reaction product mainly comprises citric acid, wherein one carboxylic group of the citric acid is esterified with one of the free hydroxylgroups of the glycerol backbone of the mono- or diglyceride. Some di- or even tri-esterified citric acid may be present in the reaction mixture, depending on the specific reaction conditions used such as temperature and reaction time. One monoglyceride molecule can also be esterified with two citric acid molecules. Thus in the present specification the term "citric acid ester of mono- and diglycerides of fatty acids" encompasses monoesters, diesters, triesters of citric acid and mixtures thereof. This term also includes esters wherein one monoglyceride is esterified with two citric acid molecules. In the present specification the ester or mixture of esters is also referred to as "ester of citric acid" or "citric acid ester".

20 The esters are for example prepared in a reaction of citric acid with monoglycerides or a mixture of mono- and diglycerides. Examples of a suitable starting mixture comprises more than 20 wt%, preferably greater than 40 wt%, more preferably from 80 to 99 wt%, more preferably 90 to 95 wt% of monoglyceride.

25 The mono- and diglycerides of fatty acids which are esterified with citric acid may be produced according to state of the art.

The citric acid esters for inclusion in the fat phase and/or the aqueous phase may be selected from the following commercial citric acid esters: GRINDSTED™ CITREM LR 30 10, GRINDSTED™ CITREM BC-FS, GRINDSTED™ CITREM N 12 and combinations thereof.

The citric acid esters for inclusion in the fat phase and/or the aqueous phase may have an iodine value from 0 to 130

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The citric acid esters for inclusion in the fat phase may have an acid value from 0 to 290. The citric acid esters for inclusion in the aqueous phase may have an acid value from 0 to 230

- 5 The citric acid esters for inclusion in the fat phase may have a saponification value from 200 to 610. Preferably the citric acid esters for inclusion in the aqueous phase may have a saponification value from 200 to 550

- The citric acid esters are fat soluble or dispersible in the fat phase. In this fat soluble or dispersible form, they are also referred to as citric acid esters in the acidic form. These fat soluble or dispersible citric acid esters can be converted into water dispersible citric acid esters by fully or partly neutralising the free carboxyl groups. This is also referred to as neutralising the citric acid ester. Bases or salts thereof can be applied for neutralising. Examples of suitable bases or salts are potassium hydroxide, sodium hydroxide, calcium hydroxide, sodium carbonate. Combinations thereof can be applied.
- 10
15

An aqueous solution of neutralised citric acid ester preferably has a pH of between 5 and 6.

- 20 The fatty acid chains of the citric acid ester of mono- and diglycerides of fatty acids can be any fatty acids. Preferred fatty acid chains are selected from the group of fatty acids having a chain length of between 4 and 24 carbon atoms. More preferably these are selected from the group of monoglycerides with fatty acids having a chain length of between 12 and 22 carbon atoms. These correspond to the fatty acids found in most well known triglyceride oils.
- 25

- Examples of suitable fatty acids are fatty acids derived from a vegetable fat such as soy bean oil, rapeseed oil, olive oil, palm oil, sunflower oil, corn oil, safflower oil, cotton seed oil, palmkernel oil, coconut oil, linseed oil, butter oil or fractions thereof, or other lauric acid oils.
- 30

- To further improve the current products, the emulsion optionally comprises from 0.1 to 5 wt% on total product weight of an emulsifier other than an ester of citric acid. Traditionally emulsifiers are present in spreadable margarines which are traditionally sold in a wrapper or a tub. Emulsifiers are generally believed to effectively increase the
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stability of an emulsion (Food science and technology, G. Hoffmann, Academic press, 1989, page 147, par A1). Examples of emulsifiers are mono- and diglycerides of fatty acids. The specific, most suitable composition is dependent on the type of emulsion (such as water in oil or oil in water) as desired.

5

Optionally, frying compositions according to the invention comprise a protein or a combination of proteins. These proteins may serve, in low amounts, for browning of the composition during heating and they may positively influence frying signal functions like foaming when the frying composition is heated in a frying pan. Suitable amounts of protein are from 0.1 to 2 wt% on total product weight.

10

Examples of suitable proteins are soy protein, dairy proteins such as whey protein, whey powder, skim milk powder, butter milk powder, Na-caseinate or combinations thereof.

15 An emulsion according to the invention preferably comprises a wt% of 30 to 98 of a triglyceride fat or a mixture of triglyceride fats (fat blend).

Most known fat blends that are suitably used in margarine or spread frying compositions were found to be suitable for products according to the invention.

20

A suitable fat blend for margarine or spreads in tubs or wrappers consists of a mixture of an oil and one or more fats. The ratio of liquid oil and fat is chosen so that after processing together with an aqueous phase, a product with suitable consistency and spreadability is obtained.

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Any edible, liquid oil and fat can be used, e.g. soybean oil, rapeseed oil, palm oil, sunflower oil, corn oil, safflower oil, olive oil, cottonseed oil, palm kernel oil, coconut oil and other lauric acid oils, butter oil and partially or fully hydrogenated fractions or interesterifications thereof.

30

In addition to the above mentioned ingredients, food products according to the invention may optionally contain further ingredients suitable for use in these products. Examples of these ingredients are sweetener materials, EDTA, spices, vitamins, bulking agents, egg yolk, stabilising agents, flavouring materials, colouring materials, acids, preserving agents, flavour compositions, vegetable particles etc. However the amount of these

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ingredients is preferably that desired characteristics of the emulsion are not severely affected by the presence of these ingredients. Therefore for example the presence of low amounts of flavour components, and/or colouring agents is tolerated. However the presence of sugars or stabilising agents, which are known to cause burning is often less preferred.

Traditionally, margarines and like products, and also butter comprise salt. Known margarines and spreads comprise varying amounts of salt, which are tuned to the consumers desires. Preferably the amount of salt is between 0.2 to 3, preferably 0.8 to 3 wt% of salt. Most preferred levels of salt are from 1 to 2.5 wt%.

Optionally, the products according to the invention comprise gas such as nitrogen, carbon dioxide or another, preferably inert gas. It has been found that such gas if present can suitably further stabilise an emulsion.

15

Generally the balance of compositions according to the invention will be water.

Products according to the invention could be prepared by one skilled in the art. For example according to one embodiment, a premix comprising all ingredients is prepared, followed by blending and mixing in order to establish a suitable emulsion. If desired the crystallisation of solid fat may be performed as a processing step in which the premix is cooled by one or more scraped surface heat exchangers. In such a step also the process of emulsification could take place. Emulsification could on the other hand as well be envisaged by other kinds of techniques as, e.g. membrane emulsification and alike.

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According to another embodiment, a separate fat phase comprising a fat blend and fat soluble or dispersible ingredients and a separate aqueous phase comprising ingredients dispersed in water are mixed.

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The resulting product is preferably stored at a temperature from 0 to 15 °C.

The citric acid ester can be added at any moment in the process, generally before cooling and filling the product in packaging material.

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It has surprisingly been found that an emulsion showing desired frying performance in low spattering, can be prepared by a process which comprises the steps of

- (i) providing an aqueous phase comprising a citric acid ester of mono- and diglycerides of fatty acids;
- 5 (ii) providing a fat phase comprising a citric acid ester of mono- and diglycerides of fatty acids, wherein the fat phase is substantially free of lecithin and monoglycerides; and
- (iii) mixing the aqueous phase and the fat phase to obtain the emulsion.

Spattering values for products prepared by this process were surprisingly found to be
 10 better than spattering values for products comprising the same amount and type of esters of citric acid, where these esters were added to the premix or to the emulsion of the fat phase and the water phase. Therefore a preferred embodiment of the invention relates to this process and an emulsion obtained by this process.

- 15 Even more preferred in the above process 0.05 to 2 wt% of said citric acid ester on total product weight is added to the fat phase in step (ii).

According to a further preferred aspect of the invention, the aqueous phase prepared in step (i) comprises from 0.05 to 3 wt% of the citric acid ester in neutralised form. This
 20 ester may be added to the aqueous phase or may be formed in situ by increasing the pH of an aqueous phase comprising the ester of citric acid in its acidic form.

In another embodiment the citric acid ester is added to the aqueous phase in a first step, which aqueous phase is mixed with a fat phase which is free of citric acid ester, in
 25 a second step.

The citric acid ester in the aqueous phase and the one in the fat phase can be of a different fatty acid composition.

- 30 It has surprisingly been found that especially frying compositions wherein citric acid ester is added to both the fatty phase and the aqueous phase of the emulsion, and the total amount of said esters is above 0.2 wt%, show satisfying spattering behaviour.

The invention will now be described by way of example only.

EXAMPLE

Determination of Bostwick Value

5 Pourability or squeezability is measured according to the standard Bostwick protocol. The Bostwick equipment consists of a 125 ml reservoir provided with a outlet near the bottom of a horizontally placed rectangular tub and closed with a vertical barrier. The tub's bottom is provided with a 25 cm measuring scale, extending from the outlet of the reservoir. When equipment and sample both have a temperature of 15°C, the reservoir
10 is filled with 125 ml of the sample after it has been shaken by hand ten times up and down. When the closure of the reservoir is removed the sample flows from the reservoir and spreads over the tub bottom. The path length of the flow is measured after 30 seconds. The value, expressed as cm per 30 seconds is the Bostwick rating, which is used as yard stick for pourability.

15

The maximum value that can be determined with this measurement is 23.

Determination of spattering value

20 The spattering behaviour of food products according to the invention was evaluated after storage of the products 8 days at 5 °C.

Primary spattering (SV1) was assessed under standardised conditions in which an aliquot of a food product was heated in a glass dish and the amount of fat spattered
25 onto a sheet of paper held above the dish was assessed after the water content of the food product had been driven off by heating.

Secondary spattering (SV2) was assessed under standardised conditions in which the amount of fat spattered onto a sheet of paper held above the dish is assessed after
30 injection of a quantity of 10 ml water into the dish.

In assessment of both primary and secondary spattering value about 25 g food product was heated in a glass dish on an electric plate set at about 205 °C. The fat that spattered out of the pan by force of expanding evaporating water droplets was caught
35 on a sheet of paper situated above the pan. The image obtained was compared with a

set of standard pictures number 0-10 whereby the number of the best resembling picture was recorded as the spattering value. 10 indicates no spattering and zero indicates very bad spattering. The general indication is as follows.

Score	Comments
10	excellent
8	good
6	passable
4	unsatisfactory for SV1, almost passable for SV2
2	very poor

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Typical results for household margarines (80 wt% fat) are 8 for primary spattering (SV1) and 5 for secondary spattering (SV2) under the conditions of the above mentioned test.

Preparation of frying product

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The principle of preparing margarine and spreads is well known to every person skilled in the art. The production of margarine is extensively described in the chapter "The Process" of Andersen's and William's book "Margarine", 2nd edition, 1965. The processing and production of spreads is described in the AOCS World Conference

15 Proceedings "Edible Fats and Oils Processing", Maastricht, October 1989, "Low Calorie Spread and Melange Production in Europe", pp. 221-227.

Methods

20 In the present examples, a Votator pilot plant was used, capacity 95 kg/hour, pressure 10-12 bar, pasteurisation 72°C, emulsion inlet temperature 40°C, A-unit 1 annular space 5 mm, rotor speed 1,000 rpm, temperature outlet set point 30.5°C, C-unit 1 volume 3 litres, rotor speed 800 rpm, temperature outlet C-unit 1 approx. 32°C, A-unit 2 annular space 3 mm, rotor speed 1,000 rpm, temperature outlet set point 19.5°C, A-unit 3

25 annular space 3 mm, rotor speed 1,000 rpm, temperature outlet set point 9.5°C, C-unit 2 volume 1 litre, rotor speed 400 rpm, temperature outlet C-unit 2 approx. 12°C and filling temperature approx. 12°C.

In process A the citric acid ester in the acidic form is added to the fat phase before the fat phase is mixed with the aqueous phase.

In process B the ester of citric acid in the neutralised form is added to the aqueous phase before the aqueous phase is mixed with the fat phase.

In process C, the citric acid ester in the acidic form is added to the fat phase and the ester of citric in the neutralised form is added to the aqueous phase before the aqueous phase and the fat phase, are mixed.

The product composition for examples 1-5 is shown in table 1.

The results in frying properties (SV1) are included in the bottom row of table 1.

TABLE 1

Ingredient	1	2	3	4	5	C1	C2
Tub fat blend ¹	69.5	69.5	69.5	69.5	69.5	69.5	69.5
Lecithin ²							0.18
Cetanol ³							0.1
GRINDSTED TM CITREM LR 10 ⁴	0.4	0.1			0.4		
GRINDSTED TM CITREM BC- FS ⁵			0.4				
Beta carotene ⁶	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Aqueous phase							
Whey powder	0.4	0.4	0.4	0.4	0.4		
Salt	0.3	0.3	0.3	0.3	0.3		0.3
GRINDSTED TM CITREM N 12 ⁷	0.4	0.1	0.4	0.4			0.4
K-sorbate	0.073	0.073	0.073	0.073	0.073		0.073
pH aqueous phase	4.7	4.7	4.7	4.7	4.7	4.7	4.7
Process	C	C	C	B	A		
Results							
SV1	8.5	8.75	8	8	5.75	0	7.75

The balance of all composition to 100% is water

1: The tub fat blend had the following N values:

N05	17.1
N10	14.6

N15	11.2
N20	8.6
N25	5.9
N30	3.8
N35	2.1

- 2: Lecithin was hydrolysed lecithin (Bolec MT) obtained from UMZ
- 3: Fractionated lecithin by fractionation of lecithin with acetone; cetinol from UMZ
- 4: Citric acid ester which is in the acidic form and fat soluble or dispersible, the
- 5 citric acid ester is esterified with a monoglyceride derived from sunflower oil
- 5: Citric acid ester which is in the acidic form and fat soluble or dispersible, the citric acid is esterified with a monoglyceride with fatty acid chain derived from fully hardened palm oil.
- 6: Beta carotene was added in the form of an 0.4 wt% solution in sunflower oil
- 10 7: Citric acid ester which is in the neutralised form and water dispersible, the citric acid is esterified with a monoglyceride with a fully hydrogenated fatty acid chain. It was added to the aqueous phase by making a premix of 20% GRINDSTED™ CITREM N 12 in 80-90°C hot water

15 Conclusions

Products wherein citric acid ester was added to both the fat phase and the aqueous phase show better spattering behaviour than products comprising lecithin (comparative example C2). Products comprising citric acid ester in the aqueous phase only (example

20 4) show improved spattering behaviour compared to products that do not comprise any anti-spattering agent (comparative example C1).

If the total amount of citric acid ester in the aqueous phase is increased from 0.4 wt% to 0.8 wt% SV1 is improved.

25

All publications mentioned in the above specification are herein incorporated by reference. Various modifications and variations of the described methods and system of

30 the invention will be apparent to those skilled in the art without departing from the scope

and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims.

CLAIMS

1. A non-pourable emulsion comprising
 - (i) an aqueous phase comprising a citric acid ester of mono- and diglycerides of fatty acids; and
 - (ii) a fat phase comprising a citric acid ester of mono- and diglycerides of fatty acids, wherein the fat phase is substantially free of lecithin and monoglycerides.
2. A non-pourable emulsion according to claim 1, wherein the ester is a citric acid ester of mono- and diglycerides of fatty acids.
3. A non-pourable emulsion according to claim 1 or 2, wherein the citric acid ester is present in the emulsion in an amount of from 0.1 to 3 wt% of the emulsion.
4. A non-pourable emulsion according to claim 1, 2 or 3, wherein the citric acid ester is present in the aqueous phase of the emulsion and the interface between the aqueous phase and fat phase in an amount of from 0.07 to 3 wt% of the emulsion.
5. A non-pourable emulsion according to any one of claims 1 to 4, wherein the citric acid ester is present in the fat phase of the emulsion in an amount of 0.05 to 2 wt% of the emulsion.
6. A non-pourable emulsion according to any one of the preceding claims wherein the fatty acid of the citric acid ester of mono- and diglycerides of fatty acids has a chain length of from 4 to 24 carbon atoms.
7. A process for the preparation of a non-pourable emulsion comprising the steps of
 - (i) providing an aqueous phase comprising a citric acid ester of mono- and diglycerides of fatty acids;
 - (ii) providing a fat phase comprising a citric acid ester of mono- and diglycerides of fatty acids, wherein the fat phase is substantially free of lecithin and monoglycerides; and
 - (iii) mixing the aqueous phase and the fat phase to obtain the emulsion.
8. A non-pourable emulsion as substantially described herein with reference to any

one of the Examples.

9. A process as substantially described herein with reference to any one of the Examples.



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Claims searched: 1-9

Examiner: Peter Trickey
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Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): A2B (BKE), C5C (CPD)

Int Cl (Ed.7): A23D 7/00; A23L 1/035

Other: Online: EPODOC, WPI, JAPIO, TXTE

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	EP 0649599 A (Sanofi) Lines 17-22 page 2	
A	DE 3221143 A (Winter) WPI abstract accession number 1983-802301 [44]	

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.

& Member of the same patent family

A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.

E Patent document published on or after, but with priority date earlier than, the filing date of this application.